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Comparison of Several Techniques for Determining Dry Deposition Flux

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16. ABSTRACT

Over the period from 1/22/81 through 5/4/82, measurements were conducted to permit comparison of several techniques for determining dry deposition flux of nitrates and sulfates. Direct flux estimates were made by using actual leaf surfaces and foliar wash and by exposing and washing three surrogate surfaces: bucket, petri dish, and cellulose filter. Indirect flux estimates were made using SSI high volume sampling along with meteorological measurements. The time scale for the direct methods was nominally one month. The indirect method used 24-hour particulate sampling and three-hour meteorological observations to calculate average flux values for the exposure periods of the direct methods. This permitted comparison of direct and indirect methods on a similar time scale.

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COMPARISON OF SEVERAL TECHNIQUES FOR DETERMINING DRY DEPOSITION FLUX

INTRODUCTION

The problem of acidic deposition is currently receiving attention from both the lay and technical communities. Acidic deposition is comprised of two components: wet and dry. Dry deposition includes all processes by which airborne contaminants are removed from the atmosphere at the surface of the earth, excluding those processes directly aided by precipitation. Dry deposition contributes substantially to the total acidic deposition burden. Thus, efforts to monitor dry deposition and to investigate its behavior will provide insight on the role that it assumes in the larger problem of acidic deposition.

The rate of dry deposition of atmospheric pollutants depends on many factors concerning the pollutants, surfaces, and atmospheric conditions. A recent workshop has examined various methods to measure dry deposition (Hicks et al., 1980) and found that a simple, accurate method for monitoring dry deposition was not available. It was felt that the direct dry deposition flux monitoring approaches now being used were deficient because their use of surrogate surfaces gave flux values which were not representative of the "natural" surfaces they were chosen to imitate. Although it is desirable to use some indirect or parameterized method to estimate dry deposition, this approach is also limited to a theoretical exercise until direct methods of monitoring dry deposition are available to provide the data for comparative validation.

The goal of this program was to determine simultaneous monthly estimates of dry deposition flux of nitrates and sulfates over a year's duration by several methods and to compare the results. Direct estimates were made by using actual leaf surfaces and foliar wash and by using three surrogate surfaces: bucket, petri dish, and cellulose

filter. Indirect estimates were made using the concentration determined by sampling and by using the deposition velocity estimated from meteorological measurements.

METHODS

Foliar Wash

A plant bed having approximate dimensions of 4 m by 5 m was fabricated. A rain-actuated cover was designed to keep the plants dry during rainy periods. This device was activated by the rain-sensor portion of the Aerochem Metrics wet/dry precipitation sampler that was also used in the study.

Ligustrum, a landscape plant common in Piedmont, North Carolina, was selected for the study. Approximately 30 plants were acquired from a local nursery. The plants were approximately 0.5 m tall and were potted in 4 L containers. Average leaf area was approximately 1 cm^2/leaf.

The plants were exposed in the plant bed for nominal 1-month periods that ran concurrently with those for other direct methods. At the end of each exposure period approximately one leaf per plant was harvested. Subsequently, the plants (minus the harvested leaves) were washed vigorously by spraying with tap water and were rinsed with deionized (DI) water. Next, a postwash leaf harvest was conducted. Harvested leaves were returned in polyethylene containers to the lab; 100 mL of DI water was added to each container; and the container was agitated for 30 minutes using a mechanical shaker. Increased shaking times of 60 and 1440 minutes were investigated to address the issues of internal leaching and adequacy of the 30-minute wash time. Appreciable increases in NO_3^- or $SO_4^=$ were not observed at the longer times.

At the conclusion of the foliar wash, aliquots of wash liquor were decanted into polyethylene bottles and refrigerated until they were subjected to NO_3^- and $SO_4^=$ analysis by Ion Chromatography (IC). All NO_3^- and $SO_4^=$ analyses were performed on a Dionex Model 14 Ion Chromatograph. Analysis conditions were as follows:

Pre-column: 3 x 150 mm anion pre-column
Separator column: 3 x 500 mm anion separator
Suppressor column: 6 x 250 mm anion suppressor
Eluent: 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3
Flowrate: 138 mL/hr
Sample size: 0.1 mL

Standards which covered the concentration range of the samples were run daily. A linear least squares fit of the standard data points (x,y) where x = concentration in μg/ml and y = peak height in mm was calculated both for NO_3^- and for $SO_4^=$; these fits were used to determine the NO_3^- and $SO_4^=$ concentrations for samples run that day. The detection limit for NO_3^- and $SO_4^=$ is approximately 0.1 μg/mL.

Quality control (QC) filter strip samples were provided by EPA to assess the quality of the IC determinations of NO_3^- and $SO_4^=$. The standard and determined values generally agreed within 5 percent. The mean "standard/determined" ratio for 35 QC samples is 1.0149 $\pm$ 0.0437 for NO_3^- and 1.0055 $\pm$ 0.0286 for $SO_4^=$. These results indicate average high biases of 1.5 percent for NO_3^- and 0.6 percent for $SO_4^=$ with corresponding precision estimates of 4.4 percent and 2.9 percent. These measures of precision also include the variability in the preparation of the EPA standards which is probably small. In addition, different-day replicate analyses of 9 QC samples were performed. These results gave precision estimates (standard deviation of difference) of 2.9 percent for NO_3^- and 3.0 percent for $SO_4^=$.

The leaves were subjected to triplicate leaf area determinations. The mean coefficient of variation (CV = 100 x standard deviation ÷ mean) of leaf area for 45 batches of harvested leaves is 0.28 percent.

Pollutant loading was determined by dividing the amount of the anion (NO_3^- or $SO_4^=$) found in the total volume of the wash liquor by the leaf area. This loading was corrected for its nonzero loading at the start of the exposure by subtracting the postwash loading determined during the previous month. The correction for $SO_4^=$ averaged 13 percent of the uncorrected loading and in 10 of 14 cases amounted to less than 12 percent. The corrected loading was then divided by the number of days for the exposure to arrive at flux in $\mu g/cm^2$ day. It should be

noted that the reported flux data based on foliar wash require the assumptions of unity leaf area index and negligible leaching of NO_3^- and $SO_4^=$ from the internal pool of these nutrients that exists within the leaves.

To determine the variability associated with leaf selection, harvesting, and washing, replicate samples were collected for five exposure periods. Comparison of loadings show excellent agreement with respective mean CV's for NO_3^- and $SO_4^=$ of 3.2 and 3.3 percent.

Bucket

An Aerochem Metrics wet/dry precipitation sampler was used with a bucket in place in the dry side only. The collector is equipped with a moisture sensor that activates a motor which moves a cover over the dry fall bucket. This sensor also activates the motorized cover for the plant bed. When the precipitation stops, the process is reversed. The sampler was modified slightly by the fabrication of a 45 cm diameter bird ring which was installed to prevent avian contamination of the samples. The bucket is made of white polyethylene, has an opening area of 641 cm^2, and is positioned at a height of approximately 1.5 m.

The bucket was exposed for nominal 1-month periods that ran concurrently with those for other direct methods. Upon return to the lab, the bucket was rinsed with 250 ml of DI water. The wash liquor was allowed to equilibrate in the bucket for 24 hours before being transferred to a polyethylene bottle for refrigerated storage prior to IC analysis. The procedure is similar to that described by Stensland et al. (1980).

Data were not collected to permit an assessment of the precision of the bucket method. Duplicate monthly exposures using a similar sampler have displayed median CV's of 11.8 and 3.7 percent for NO_3^- and $SO_4^=$ (Parkhurst et al., 1981). In the current study, close agreement was found for the dry fall flux values based on bucket sampling and those based on petri dish sampling. The open petri dish estimates were quite precise with average CV's of 6.9 and 3.9 percent. It is, therefore, expected that the precision of dry fall flux based on

bucket sampling in the current study is 10 percent for NO_3^- and 5 percent for $SO_4^=$.

Pollutant loading was determined by dividing the amount of the anion (NO_3^- or $SO_4^=$) found in the total volume of the wash liquor by the opening area of the bucket (641 cm^2). The loading was then divided by the duration of the exposure in days to arrive at flux in $\mu g/cm^2$ day.

Open Petri Dishes

Polystyrene petri dishes having an area of 60.8 cm^2 were suspended at leaf level in the plant bed and used as dryfall collectors. The dishes were exposed for nominal 1-month periods that ran concurrently with those for the other direct methods. Upon return to the lab, the dishes were rinsed with 25 mL of DI water. The subsequent procedure was similar to that described above for the bucket.

Replicate exposures were conducted; however, in some cases the duplicate dish was dislodged from its support and lost due to high winds. Dry fall flux values based on petri dish sampling are very precise: the average CV's (n=7) for NO_3^- and $SO_4^=$ are 6.9 and 3.9 percent.

Pollutant loading was determined by dividing the amount of the anion (NO_3^- or $SO_4^=$) found in the total volume of the wash liquor by the opening area of the dish (60.8 cm^2). The loading was then divided by the duration of the exposure in days to arrive at flux in $\mu g/cm^2$ day.

Filter Petri Dishes

Discs of Whatman 41 cellulose filter paper having an area of 60.8 cm^2 were attached to the inside surface of the petri dishes described earlier. These petri dishes containing filter paper were suspended in the plant bed beside the open petri dishes and were exposed for nominal 1-month periods concurrently with the other direct methods. The same procedure as described for the open petri dish was used for washing the surface.

Replicate exposures were conducted, and as with the open petri dishes, some samples were lost due to winds. The results indicated good precision with average CV's (n=5) for NO_3^- and $SO_4^=$ of 7.4 and 10.8 percent. Pollutant loading and flux were calculated using the same approach as was described earlier for the open petri dishes.

Concentration

High volume samplers equipped with Andersen Model 7000 Size Selective Inlets (SSI) were used to sample airborne particulate smaller than 15 μm in diameter at a height of 1.5 m. Four samplers were employed with their timers set up to permit three days of unattended sampling. Monthly flow rate audits using an EPA-supplied reference flow orifice generally showed agreement to within 10 percent and in 28 of 39 cases showed agreement to within 7 percent. To permit an assessment of the short-term precision associated with suspended particulate (SP), NO_3^-, and $SO_4^=$ data from the SSI samplers, duplicate samples were collected on each of five consecutive days. The average respective CV's were 2.8, 2.5, and 3.0 percent. This suggests that the precision of the SSI data in the current study is 3 percent.

Gaseous HNO_3 and SO_2 are present in ambient air and may interact with filter-type collection surfaces to form particulate NO_3^- and $SO_4^=$. At the 1 ppb level assuming complete retention, artifact NO_3^- and $SO_4^=$ particulate levels of 2.5 and 3.9 $\mu g/m^3$ would result. The desire to eliminate artifact NO_3^- and $SO_4^=$ formation from gaseous HNO_3 and SO_2 on alkaline glass fiber filters led to the selection of Pallflex QAST quartz filters. The pH of the aqueous extract from these filters was found to be 6.9. Replicate dynamic and static blanks (n=9) revealed low background levels of NO_3^- and $SO_4^=$: 21 ± 18 μg NO_3^-/filter and 299 ± 28 μg $SO_4^=$/filter. These mean values were used as background values to correct SSI NO_3^- and $SO_4^=$ data.

Although it is believed that Quartz filters provide accurate $SO_4^=$ data, the reliability of the NO_3^- data is questionable. Particulate NO_3^- measurements are subject to both positive and negative biases depending on the nature of the filter medium, the sampling duration, the acid-base character of other collected materials, and the gas phase concentrations of HNO_3 and NH_3 (Appel and Tokiwa, 1981). In the current study, the NO_3^- data generally showed low and variable

concentrations. As a result of the above considerations, NO_3^- flux estimates in the current study should be viewed as suspect.

SSI samples were collected on each working day from 4-27-81 until 4-2-82. Except for two periods, 24-hour sampling from midnight to midnight was used. For the two periods beginning on 4-27-81 and on 7-30-81, two samples were collected on each working day (1000-1700 and 1700-1000 hours) to investigate day-night differences.

Quartz filters were returned to the lab for analysis in polyethylene bags. A 1" x 8" strip was cut from the center of the filter (1" x 7" of exposed filter) and placed in a 50 mL polyethylene beaker. Twenty mL of the 0.003M $NaHCO_3$/0.0024M Na_2CO_3 eluent was pipetted into the beaker, completely immersing the filter. The samples were ultrasonicated for 30 minutes and allowed to stand overnight. The desorption efficiency of this procedure has been checked and found to be complete. The solution was then decanted and injected directly into the IC for NO_3^- and $SO_4^=$ determination.

The pollutant concentration was calculated by correcting the amount of anion (NO_3^- or $SO_4^=$) found on the filter for the background levels found on the blank filters. This amount of anion (in units of μg) is divided by the total volume of air drawn through the filter to arrive at concentrations in $\mu g/m^3$.

Estimated Deposition Velocity

The downward deposition velocity, v_d, for sulfate particles at an altitude z can be approximated (Sheih et al., 1979) by

$$v_d = ku*/(\ln z/z_o + ku*r_p - \psi_c) \qquad (1)$$

where k is von Karman's coefficient (0.40); $u*$ is the friction velocity ($ku/[\ln z/z_o - \psi_m]$); u is the wind speed at height z; z_o is the surface roughness length characteristic of the measurement location; r_p is the surface "resistance" to particulate deposition; and ψ_c and ψ_m are the atmospheric stability correction functions for the aerosol concentration and the momentum. Estimates of the deposition velocity are possible once the terms of (1) are known.

At the RTI site, winds at 10 m were measured continually and averaged for five minute periods. These five minute averages were further averaged to give mean hourly wind speeds. The surface roughness length for the site was estimated as 30 cm, based on data for grassland and woodlands (Sheih et al., 1979). However, neither direct nor indirect measurements of the properties needed to compute ψ_c or ψ_m were available at the site. Consequently, alternative estimates of these functions were necessary.

The stability correction functions depend upon the stratification of the atmospheric surface boundary layer. That stratification at the point z can be related to the dimensionless ratio z/L, where $L = (-u_*^3 C_p \rho T/kgH)$ is the Monin Obukhov scale length (C_p, ρ, and T are the specific heat at constant pressure, density, and temperature of the air; g is the acceleration of gravity; and H is the vertical heat flux).

For this study, we assumed that the flux of material has the same dependence on z/L as does the heat flux, so the stability correction term ψ_c has the same functional form as that for the heat flux. These correction functions are given by

$\psi_m = \psi_c = -5z/L$ for $0<z/L$ (i.e. stable layer) and by

$\psi_m = \exp\{0.032 + 0.448 \ln(-z/L) - 0.132 [\ln(-z/L)]^2\}$ for $0>z/L$ and

$\psi_c = \exp\{0.598 + 0.390 \ln(-z/L) - 0.090 [\ln(-z/L)]^2\}$ for the unstable case.

Atmospheric stability has been classified by Pasquill (1962) based on wind speed and solar insolation during the daylight and by wind speed and cloud cover at night. Turner (1964), recognizing that solar insolation was not routinely measured or reported, modified Pasquill's classification, using time of day and cloud data (amount and height) to form a radiation index. Stability classes based on that index and wind

speed have been used to quantify stability for atmospheric dispersion estimates. Golder (1972) developed nomograms relating 1/L and z_o with the Pasquill and the Turner stability classification schemes. For each stability category and z_o there exists a range of values of 1/L. The approximate midpoint of the range for a given stability class was chosen as representative for that class. Typical values for the type and stability class are given in Table 1. Consequently, once the stability type (Turner or Pasquill) and class are known, L is estimated, the stability correction functions can be calculated, and the friction velocity u* can be computed.

The remaining term needed to compute the deposition velocity is r_p, the "resistance" to particulate deposition by the surface layer. In effect, this term represents the particle's ability to penetrate the laminar sublayer of the surface and remain on the surface without reentrainment into the air. As r_p increases, deposition velocity decreases. Wesley and Hicks (1979) have found that r_p for sulfate particles is approximately 1.0 sec/cm. In the current study that value was adopted and was assumed to be constant for both NO_3^- and $SO_4^=$.

Typical values of other terms in the denominator of (1) are of the same magnitude as kr_p u*. The small value of the resistance term leads to deposition velocities of approximately 0.5 cm/sec. This is larger than the commonly used value of 0.1 cm/sec.

A comparison of the effects of the stability classification scheme was conducted for a one week period during July 1981. Deposition velocities were computed for each hour during the period, using both schemes. The Turner method used mean hourly wind speeds measured at the RTI site and cloud amount and height data from observations at the Raleigh-Durham Airport (RDU), located approximately 10 km SE of RTI. The Pasquill method used the same wind data and the onsite mean hourly insolation to determine daytime stabilities and the cloud data from RDU

Table 1. Typical values of L for Pasquill and Turner stability classes

Stability Class		L	
		Pasquill	Turner
Very Unstable	A	-10	-8
Moderately Unstable	B	-22.7	-14
Slightly Unstable	C	-83.3	-40
Neutral	D	1000	1000
Slightly Stable	E	100	40
Moderately Stable	F	20 *	15
Very Stable	G	*	5

* Classes F and G are treated as one class by Pasquill.

to determine nocturnal stabilities. The methods were in good agreement, with the Turner method giving an average deposition velocity about 10 percent lower than the Pasquill method. Further examination showed that the mean deposition velocity for the week changed by less than 5 percent if 3-hour rather than hourly data were used.

Since the error of using 3-hourly data is less than the difference in deposition velocity by means of different stability classes, and since it is convenient to use the 3-hourly observations of sky conditions as compiled in the Local Climatological Data Monthly Summary for RDU, 3-hourly evaluations of v_d were made for each day of the study starting at 0100 EST. The Turner scheme was chosen to evaluate the stability class because it required fewer input data and used the same type of data at all times over a 24-hour day.

Eight deposition velocities were estimated for each day of the study. These data were used to determine the mean deposition velocities at a height of 1.5 m for the SSI sampling intervals. The intervals normally ran from midnight to midnight; however, for the two 1-month periods beginning on 4-27-81 and 7-30-81, two SSI samples were collected each day: between 1000 and 1700, and between 1700 and 1000.

Flux Estimates

Dry deposition flux estimates (F) in units of $\mu g/cm^2$ day were made using (2).

$$F = v_d C \qquad (2)$$

This relationship says that for a species, flux is simply the product of the deposition velocity, v_d, and the concentration of that species, C. In the present study deposition velocity was estimated from meteorological measurements, and the species concentration was determined by SSI sampling.

Caveats

None of the methods employed in the present study can be considered developed to the point of having an accepted protocol or interpretation assignable to the resulting data. Consequently, the results

may be open to a variety of interpretations. For the most part, the following points are recognized, but their influence on the results cannot be assessed at this time.

- Leaves are subject to leaching of nutrients from the internal pool. They are also subject to a variety of physiological responses to environmental stresses. These responses are likely to depend on the age as well as the species of plant. Accumulation and run-off of the first drops of rain (before the cover has completely closed), of fog water, and of dew may act to cleanse the leaf surface and act as a low bias. The presence of a frame and cover near the plants may alter the air flow and the resulting deposition. Ligustrum leaves may not be representative of most natural surfaces.

- Aerosols may be reintrained after collection. Collection of aerosols may be biased according to the size distribution of the chemical species under consideration. For example, the particulate catch of the bucket and other "open container" type samplers may be biased toward large particles.

- Filter sampling for NO_3^- using a flow sampler may be subject to both positive and negative artifacts. The deposition of SO_2 and HNO_3 and retention as $SO_4^=$ and NO_3^- may act as high biases to to direct estimates of deposition. Although this would apply to all surfaces, the extent would likely depend on the type of surface.

- Indirect flux estimates involve data collected over different time scales. Furthermore, the surface roughness length and the surface resistance to deposition were assumed and were assumed to be constants.

RESULTS

General

Average concentrations of SP, NO_3^-, and $SO_4^=$ for each exposure period are displayed in Figure 1. The SP and $SO_4^=$ data behave similarly and are significantly correlated at the 0.001 level with a correlation coefficient of 0.94. Sulfate and NO_3^- show opposing trends and have a negative correlation coefficient of -0.58.

The study-wide average of the exposure period average SP, NO_3^-, and $SO_4^=$ data are 29.6, 0.139, and 7.20 $\mu g/m^3$. On the average,

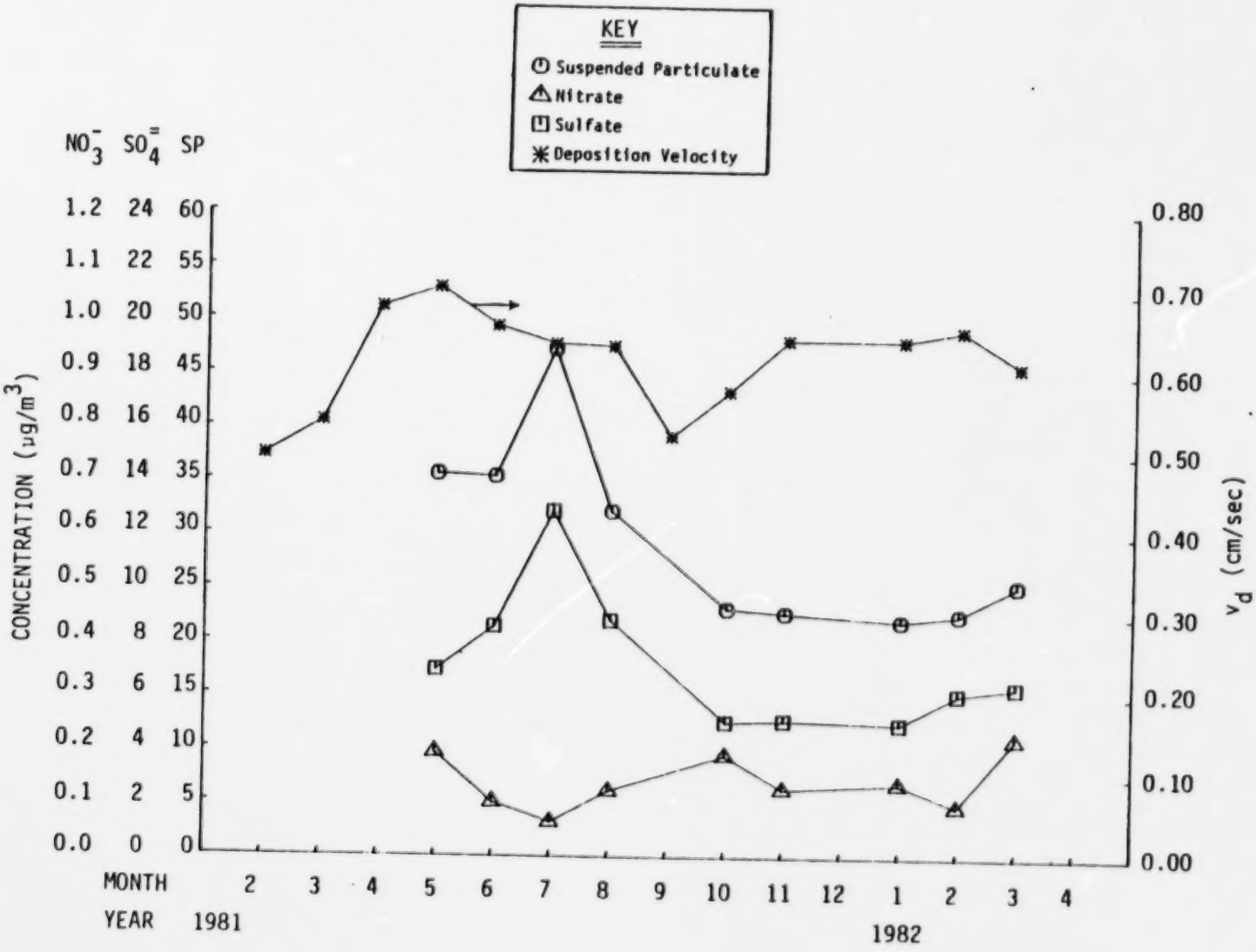

Figure 1. Average calculated deposition velocity and nitrate, sulfate, and suspended particulate concentrations over the study period.

NO_3^- comprises only 0.5 percent of the SP, while $SO_4^=$ accounts for 24 percent. Both the SP and the $SO_4^=$ data reflect summertime maxima which exceed their study-wide averages by over 50 percent.

The study-wide average of the respective exposure period CV's are 36, 105, and 50 percent. Thus, on a relative basis, NO_3^- concentrations are appreciably more variable across days than either SP or $SO_4^=$ concentrations. This variability may be reflecting previously noted sampling artifacts for NO_3^-.

Average deposition velocities at 1.5 m for each exposure period are also displayed in Figure 1. A seasonal trend in v_d is not apparent from the figure. The study-wide average of the exposure period average v_d is 0.62 cm/sec. The study-wide average of the respective exposure period CV's is 21 percent.

Day-Night Comparisons

During two sampling periods, two SSI samples were collected on each day between 1000 and 1700 and between 1700 and 1000. These data were examined for day-night differences in SP, NO_3^-, and $SO_4^=$. Data for the first sampling period (4/27/81 - 6/03/81) displayed paired mean (n=25) day-night ratios of 1.48 $\pm$ 0.52 for SP, 1.76 $\pm$ 1.19 for NO_3^- and 1.15 $\pm$ 0.62 for $SO_4^=$. Results for the second period (7/30/81 - 8/28/81) yielded ratios of 1.18 $\pm$ 0.48 for SP, 1.43 $\pm$ 0.83 for NO_3^-, and 1.40 $\pm$ 0.66 for $SO_4^=$. It should be noted that nitrate concentrations were too low to permit a meaningful analysis. For SP and $SO_4^=$, these results indicate that daytime values exceed nighttime values. The magnitude of this exceedance is clouded by the variability of the data. Statistical tests show this exceedance to be significant at the 1% level for the May SP data, at the 5% level for the August $SO_4^=$ data, and at the 10% level for August SP data; but, it is not significant at the 10% level for the May $SO_4^=$ data.

Deposition velocities were estimated for day and nighttime periods. These results were used along with measured $SO_4^{=}$ concentration data to determine $SO_4^{=}$ flux values. Mean deposition velocities, $SO_4^{=}$ concentrations, and $SO_4^{=}$ fluxes as well as paired day-night ratios for the May and for the August sampling periods are presented in Table 2. These results indicate that the daytime v_d (approximately 0.9 cm/sec with a CV of 5 percent) is less variable than the corresponding nighttime value (approximately 0.5 cm/sec with a CV of 38 percent). Examination of day-night ratios shows the daytime deposition velocity to be approximately a factor of two larger than the nighttime value; whereas, the daytime $SO_4^{=}$ levels exceed the nighttime levels by only 15-40 percent. As a result, the magnitude of the flux is very sensitive to time of day with a major portion of the variability accounted for by the variability of the deposition velocity.

NO_3^{-} and $SO_4^{=}$ Flux

Nitrate and sulfate flux values as determined for each exposure period are given in Table 3. Inspection of the study-wide mean values indicates that NO_3^{-} flux values range from 0.008 to 0.17 $\mu g/cm^2$ day, with foliar wash, bucket, and open petri dish determinations generally agreeing within a factor of 4. Sulfate flux values range from 0.019 to 0.40 $\mu g/cm^2$ day, with a factor of 4 agreement for calculated flux, bucket, open petri dish, and filter petri dish determinations. Mean NO_3^{-} flux results are ordered according to the method used: filter petri dish> bucket> open petri dish> foliar wash > calculated flux. The ordering for the $SO_4^{=}$ flux is as follows: calculated flux > filter petri dish > bucket > open petri dish > foliar wash. It is interesting to note that the lowest average NO_3^{-} flux is based on calculated flux, while the highest average $SO_4^{=}$ flux is also based on calculated flux. The low NO_3^{-} flux may be reflecting a previously mentioned NO_3^{-} sampling artifact.

The NO_3^{-} and $SO_4^{=}$ flux data over the course of the study period are depicted graphically in Figures 2 and 3. Several of the

Table 2. Day-night analysis of $SO_4^{=}$, v_d, and flux

		04/27/81 - 06/03/81[a]			07/30/81 - 08/28/81[a]		
		$\bar{X}$	SD	CV	$\bar{X}$	SD	CV
Day	$SO_4^{=}$, $\mu g/m^3$	7.18	2.86	40	11.04	6.67	60
	v_d, cm/sec	0.903	0.036	3.9	0.875	0.049	5.6
	Flux, $\mu g/cm^2 day$	0.560	0.221	39	0.840	0.512	61
Night	$SO_4^{=}$, $\mu g/m^3$	6.87	2.58	38	8.62	5.50	64
	v_d, cm/sec	0.602	0.197	33	0.479	0.206	43
	Flux, $\mu g/cm^2 day$	0.345	0.155	45	0.323	0.240	74
Paired Day-night Ratios[b]	$SO_4^{=}$	1.15	0.62	54	1.40	0.66	47
	v_d	1.77	0.89	50	2.36	1.63	69
	Flux	1.99	1.12	58	3.02	2.01	67

[a] The mean, $\bar{X}$, and the standard deviation, SD, take on the units of the appropriate parameter; however, the coefficient of variation is always expressed as percent.

[b] Ratios are dimensionless.

Table 3. Nitrate and $SO_4^{=}$ flux values (in $\mu g/cm^2$ day) for each exposure period

Exposure Period	Month	Foliar Wash		Calculated		Bucket		Open Petri Dish		Filter Petri Dish	
		NO_3^-	$SO_4^{=}$	NO_3^-	$SO_4^{=}$	NO_3^-	$SO_4^{=}$	NO_3^-	$SO_4^{=}$	NO_3^-	$SO_4^{=}$
01/22 - 02/24/81	2	0.0125	0.0145	---	---	0.0683	0.0713	---	---	---	---
02/24 - 03/26/81	3	0.0088	0.0165	---	---	0.0684	0.0597	---	---	---	---
03/26 - 04/27/81	4	0.0299	0.0180	---	---	0.0862	0.0879	---	---	---	---
04/27 - 06/03/81	5	0.0089	0.0314	0.0120	0.424	0.0295	0.1228	---	---	---	---
06/03 - 06/30/81	6	0.0141	0.0272	0.0057	0.488	0.0167	0.0753	---	---	---	---
06/30 - 07/30/81	7	0.0044	0.0256	0.0035	0.709	0.0091	0.1092	---	---	---	---
07/30 - 08/28/81	8	0.0093	0.0204	0.0067	0.483	0.0218	0.0815	0.012	0.058	0.125	0.138
08/28 - 10/01/81	9	0.0136	0.0155	---	---	0.0225	0.0713	0.015	0.052	0.105	0.113
10/01 - 11/04/81	10	0.0197	0.0172	0.0095	0.252	0.0538	0.0909	0.036	0.062	0.203	0.196
11/04 - 12/21/81	11	0.0024	0.0044	0.0071	0.283	0.0250	0.1098	0.021	0.085	---	---
12/21 - 01/29/82	1	0.0005*	0.0136	0.0076	0.277	0.0141	0.1116	0.0087	0.103	0.165	0.193
01/29 - 03/03/82	2	0.0067	0.0071	0.0054	0.345	0.0232	0.0891	0.017	0.083	0.178	0.162
03/03 - 04/02/82	3	0.0126	0.0255	0.0117	0.337	0.0280	0.1514	0.018	0.137	0.211	0.229
04/02 - 05/04/82	4	0.0134	0.0229	---	---	0.0907	0.1650	0.065	0.114	0.176	0.216
n		14	14	9	9	14	14	8	8	7	7
Mean		0.0112	0.0186	0.0077	0.400	0.0398	0.0998	0.024	0.087	0.166	0.178
SD		0.0074	0.0076	0.0029	0.145	0.0278	0.0307	0.018	0.030	0.039	0.042
CV (percent)		66	41	37	36	70	31	77	34	23	24

* Estimated based on MDC for NO_3^-.

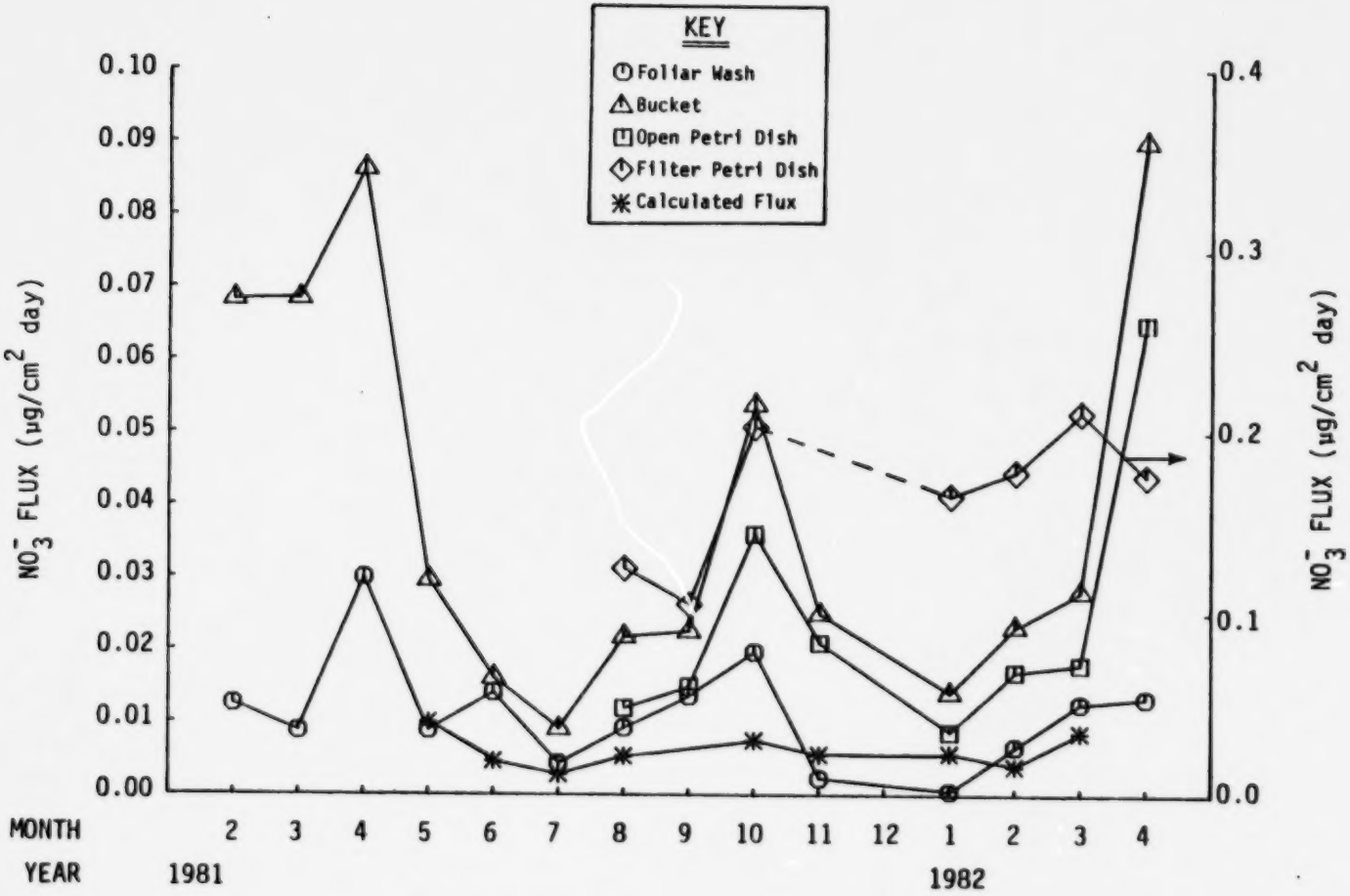

Figure 2. Nitrate flux data over the study period as determined by various methods.

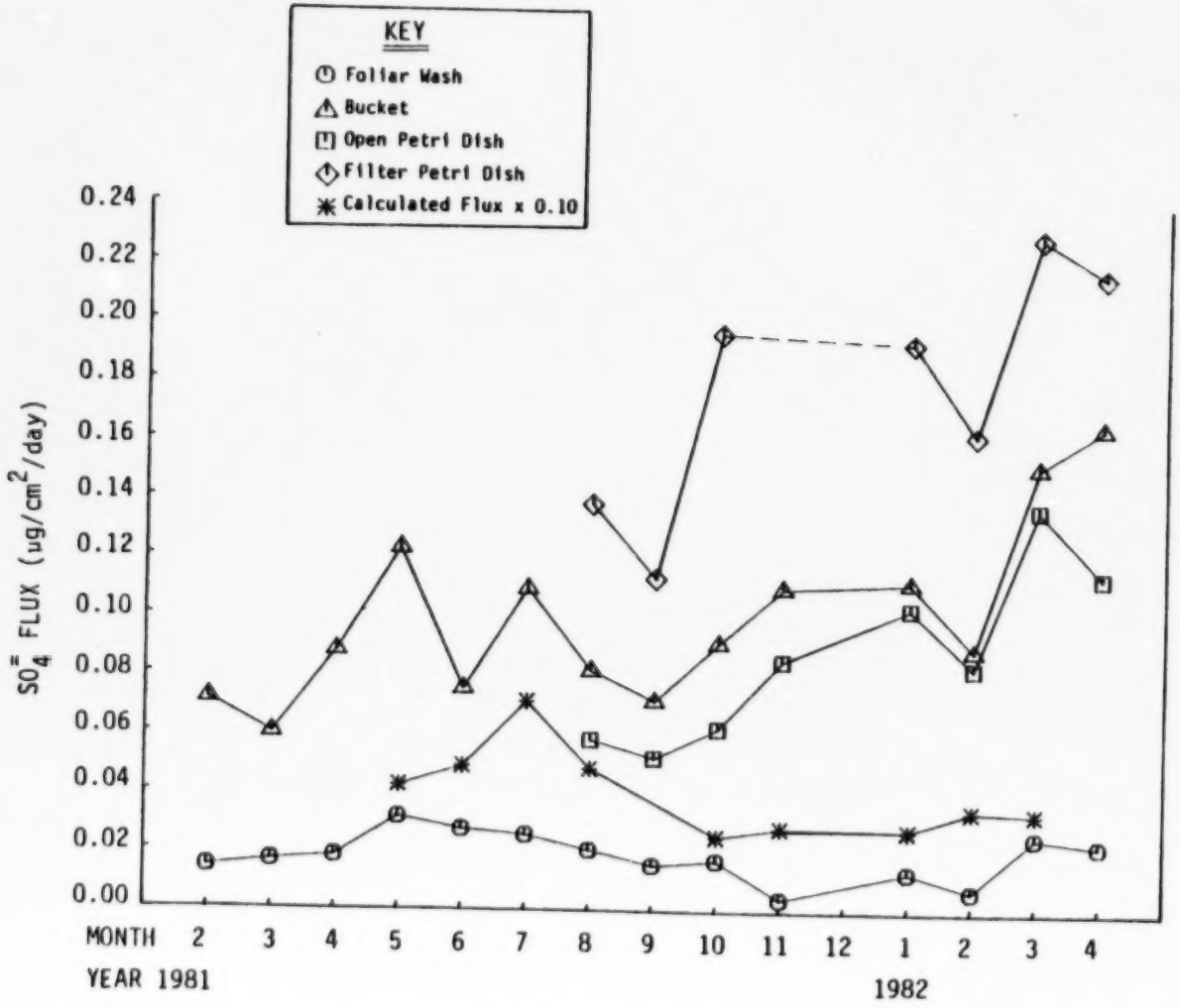

Figure 3. Sulfate flux data over the study period as determined by various methods.

methods show apparent correlation. All of the NO_3^- flux estimates show similar trends while for $SO_4^=$ flux, the bucket, open petri dish and filter petri dish methods show similar behavior. These data were subjected to correlation analysis. The results shown in Table 4 reveal significant correlation between the bucket and the open petri dish, with correlation coefficients of 0.99 for NO_3^- and 0.91 for $SO_4^=$. In addition, correlation coefficients exceeded 0.80 in two other cases, both for $SO_4^=$: bucket vs. filter petri dish and open petri dish vs. filter petri dish.

Ratios of Flux: Method to Method

Ratios of fluxes based on the various methods were determined for each exposure period. The mean bucket-to-foliar wash ratio and CV are 5.7 and 122 percent for NO_3^- and 6.9 and 83 percent for $SO_4^=$. As indicated by the CV's, the variability is substantial, so median values were identified. Based on these results, bucket estimates exceed foliar wash estimates by approximately 3 for NO_3^- and 5 for $SO_4^=$.

Bucket and open petri dishes provide comparable estimates of dry deposition. Bucket estimates on the average exceed open petri dish estimates of NO_3^- and $SO_4^=$ flux by factors of 1.5 and 1.3. In addition, this agreement is relatively constant, with CV's of 13 percent in both cases.

The filter petri dish estimates of NO_3^- and $SO_4^=$ deposition were appreciably larger than estimates based on foliar wash, the open petri dish, or the bucket. For example, the presence of the filter paper resulted in an enhancement of a factor 7.1 (CV=55%) in NO_3^- deposition and a factor of 2.2 (CV= 23%) in $SO_4^=$ deposition over the estimates based on the open dish. As indicated by the CV's, the enhancement factor is relatively constant for $SO_4^=$ but not for NO_3^-.

Ratios of Flux: NO_3^- to $SO_4^=$

Ratios of NO_3^- to $SO_4^=$ for the various methods were determined for each exposure period. These results are shown in Figure 4. For each of the methods the NO_3^- to $SO_4^=$ ratios on the average fall between 0.25

Table 4. Correlation coefficients for estimates of NO_3^- and $SO_4^=$ flux

	Filter Petri Dish		Open Petri Dish		Bucket		Calculated	
	NO_3^-	$SO_4^=$	NO_3^-	$SO_4^=$	NO_3^-	$SO_4^=$	NO_3^-	$SO_4^=$
Foliar Wash	0.20	0.47	0.50	0.35	0.63	0.32	0.37	0.56
Calculated	0.70	-0.68	0.36	-0.24	0.59	-0.15		
Bucket	0.34	0.86	0.99	0.91				
Open Petri Dish	0.34	0.84						

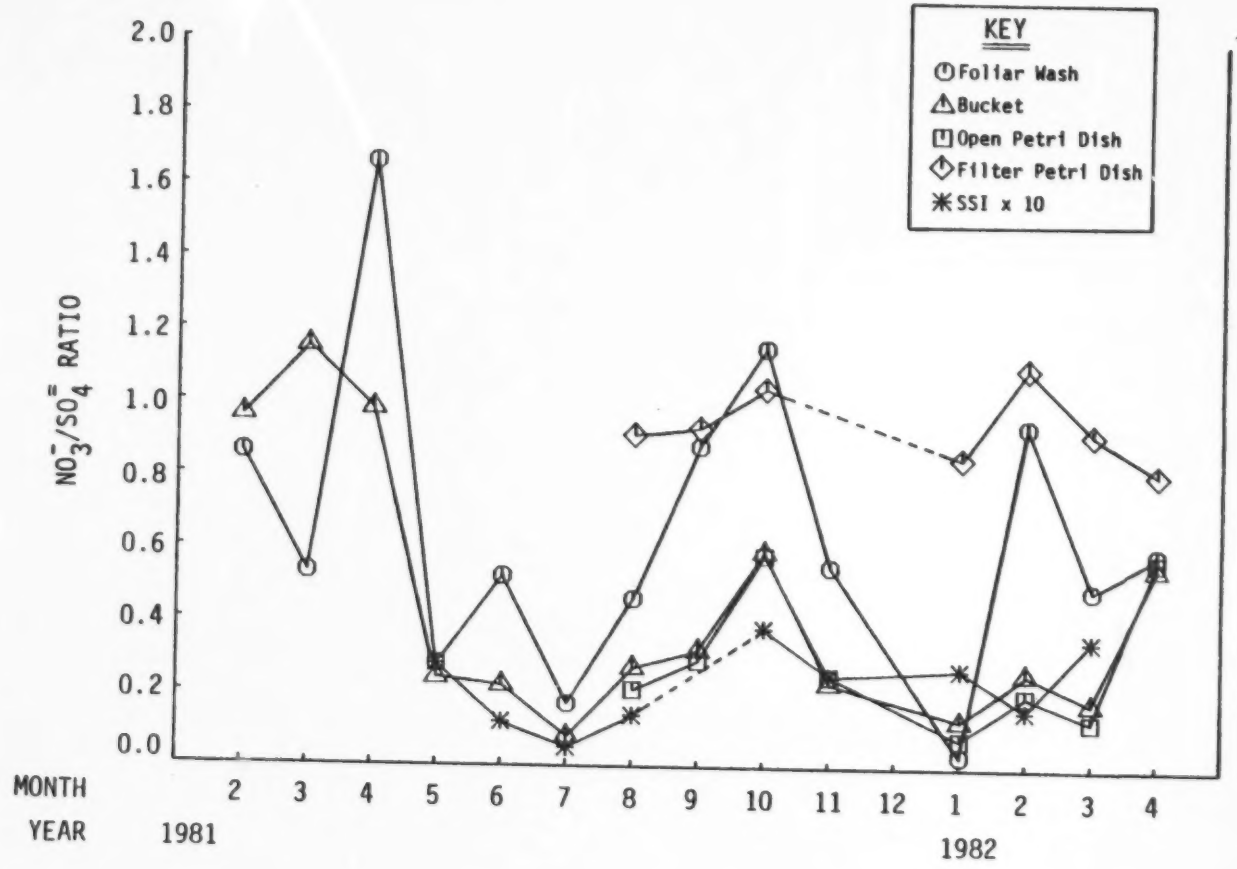

Figure 4. Nitrate to sulfate ratio over the study period as determined by various methods.

and 1.0 except for the SSI data which averages 0.022. This suggests that NO_3^- and $SO_4^=$ are deposited in relatively consistent proportions on on the four surfaces employed in the study. Nitrate and $SO_4^=$ however were not collected and retained in the same proportions on quartz filters, and retained NO_3^- appears to be biased low in comparison to the other methods. This discrepancy may be due to particulate NO_3^- sampling artifacts noted previously. The apparent bias may be due to volatilization of collected particulate NO_3^- from the quartz filter surface, or it may be due to deposition of HNO_3 and retention as NO_3^- on the four deposition surfaces.

With the exception of the filter petri dish, the other methods show similar trends in NO_3^- to $SO_4^=$ ratio over the duration of the study. The variability of bucket and the open petri dish NO_3^- to $SO_4^=$ ratio data is considerable; nevertheless, the data points are almost coincident and have a correlation coefficient of 0.99. In contrast, the ratio for the filter petri dish method is rather constant around a mean value of 0.94. Since the filter was made of cellulose and since cellulose has an ability to retain HNO_3, it is likely that the enhanced NO_3^- resulted from the deposition of gaseous HNO_3 as well as any particulate nitrate that may have been present. In addition, the rough surface of the filter probably enhanced retention of particulate nitrate and sulfate in comparison to the smoother surfaces of the leaves, petri dish, and bucket.

SUMMARY AND CONCLUSIONS

Over the period from 1/22/81 through 5/4/82, measurements were conducted to permit comparison of several techniques for determining dry deposition flux of nitrates and sulfates. Direct flux estimates were made by using actual leaf surfaces and foliar wash and by exposing and washing three surrogate surfaces: bucket, petri dish, and cellulose filter. Indirect flux estimates were made using SSI high volume

sampling along with meteorological measurements. The time scale for the direct methods was nominally one month. The indirect method used 24-hour particulate sampling and 3-hour meteorological observations to calculate average flux values for the exposure periods of the direct methods. This permitted comparison of direct and indirect methods on a similar time scale.

Mean NO_3^- flux results are ordered according to the method used: filter petri dish> bucket> open petri dish> foliar wash> calculated flux. The ordering of the $SO_4^=$ flux is as follows: calculated flux> filter petri dish> bucket> open petri dish> foliar wash.

Several methods of determining dry deposition flux show apparent correlation. Three comparisons for $SO_4^=$ had correlation coefficients exceeding 0.80: bucket vs. open petri dish; bucket vs. filter petri dish; and open petri dish vs. filter petri dish. One comparison for NO_3^- had a correlation coefficient exceeding 0.80. Comparisons of the bucket and the open petri dish showed correlation coefficients of 0.99 for NO_3^- and 0.91 for $SO_4^=$. Although the various methods of determining flux showed similar trends, with one exception, correlative comparison of results do not support the development of regression-type predictive relationships between the methods. This is especially true for the relationships between deposition on surrogate surfaces and deposition on leaves. It should be noted that in view of the divergence between fluxes based on the smooth plastic surfaces and the filter petri dish method, it is reasonable to expect a wide divergence among plant surfaces of different species. Furthermore, factors such as plant age, local climatology, and season are also expected to influence the deposition to natural surfaces. Results of the present study suggest that the apparent dry deposition to surrogate surfaces was not representative of that to living Ligustrum leaves. The results do not indicate the degree to which Ligustrum leaves are representative of natural surfaces.

Data were collected during two one-month intensive sampling periods to permit examination of day-night effects. Deposition

velocities and ambient $SO_4^{=}$ concentrations were determined for day and night periods. These data were used to calculate flux for the corresponding periods. The magnitude of the flux was found to be very sensitive to the time of day under consideration with the daytime fluxes exceeding the nighttime values by a factors of 2 to 3. Most of the exceedance results from a day-to-night enhancement of deposition velocity, not $SO_4^{=}$ concentration.

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